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## ONR LONDON CONFERENCE REPORT

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FIRST INTERNATIONAL CONFERENCE ON MATRIX ISOLATION  
SPECTROSCOPY

R.R. SMARDZEWSKI \*

22 MARCH 1978

\*Naval Research Laboratory, Washington, DC

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>This report discusses the content of several papers presented at the First International Conference on Matrix Isolation Spectroscopy, held on 21-24 June 1977 in West Berlin, FRG. A brief discussion of the technique of matrix isolation spectroscopy is included.</p>		

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First International Conference on  
Matrix Isolation Spectroscopy

The First International Conference on Matrix Isolation Spectroscopy, 21-24 June 1977, West Berlin, Germany, was, by all accounts, a highly stimulating and informative meeting. A variety of subjects was covered in numerous oral and poster sessions.

Matrix isolation spectroscopy embodies a technique that is especially suited to the isolation and characterization of short-lived chemical intermediates, particularly in highly energetic reaction sequences. The species of interest (molecule, radical, ion, metal atom cluster) is generated and trapped in an inert and usually transparent matrix at cryogenic temperatures (<20 K) and subsequently examined by appropriate spectroscopic methods (ir, Raman, uv-vis, fluorescence, ESR, etc.). In such an environment, the matrix-isolated species will exhibit molecular constants similar to those in the gas phase since the inert gas atoms of the matrix perturb the species very slightly while keeping association/polymerization to a minimum. Furthermore, since nearly all vibrational transitions in matrix spectra originate from the ground state and free molecular rotation is unlikely, spectra are considerably simplified and more readily yield fundamental information concerning structure and bonding.

The opening address of the Conference, presented by Prof. George C. Pimentel (Univ. of Calif., Berkeley), the unofficial "father" of matrix isolation spectroscopy, highlighted such new areas as kinetics in matrices, ir-induced reactions, and chemiluminescent reactions in cryogenic matrices.

Dr. M. Poliakoff and the group at the Univ. of Newcastle upon Tyne UK, described some elegant ir laser-induced photolysis reactions in matrices using a tunable, spin-flip ir laser. These first examples of selective ir laser-induced reactions in the solid state displayed both isotopic and stereochemical selectivity.

Drs. L. Andrews (Univ. of Virginia) and M.E. Jacox (NBS, Washington) described several studies using a windowless-discharge photolysis lamp to generate and isolate such species as ions ( $\text{CF}_3\text{CL}^+$ ,  $\text{HCCl}_2^+$ ,  $\text{HCCC}_2^-$ ,  $\text{CCl}_3^+$ ) and radicals ( $\text{CF}_3$ ,  $\text{CF}_2$ ) in inert cryogenic matrices. There was some question, however, as to the exact nature of the transfer of energy from the discharge to the matrix, (i.e., radiation and/or argon metastables?).

Drs. D.M. Kolb (Fritz Haber Inst., Berlin), F. Forstmann (Freie Univ., Berlin), B. Meyer (Univ. of Washington, Seattle), D. Nagel (Univ. of Hamburg), M. Jakob (Univ. of Munich), and W. Schulze (Fritz Haber Inst., Berlin) presented a variety of interpretations on the spectra of atoms (metal or otherwise) in matrices and the role of environmental influences. Along these same lines, Drs. B. Meyer (Univ. of Washington), T. Welker (Max Planck Inst., Stuttgart), and L. Andrews (Univ. of Virginia) illustrated

both an overview as well as specific examples of metal clusters in matrices. Specifically, Welker obtained the optical absorption spectra of matrix-isolated silver aggregates and microcrystals, while Andrews investigated the optical absorption and laser-excited fluorescence spectra of the potentially important Ca<sub>2</sub> Van der Waals molecule. Prof. G.A. Ozin and members of his group from the University of Toronto delivered a series of lectures dealing with the reactions of metal atoms (Ni, Pd, Rh) with elementary olefins such as ethylene. A number of lectures were also presented on the isolation and spectroscopic characterization (infrared, Raman) of binary metal halides by Drs. A. Lowenschuss and A. Givan (Hebrew Univ., Jerusalem), J.S. Ogden (Univ. of Southampton, Southampton, UK) and J.S. Shirk (IIT, Chicago).

A number of matrix ESR papers were communicated. Prof. W. Weltner, Jr. (Univ. of Florida) presented an extensive review of his and other ESR studies of high temperature and interstellar molecules. Dr. D. Mihelcić (Inst. für Atmosph. Chemie, Jülich) had applied the technique to some air-borne measurements of free radicals in the atmosphere. Dr. P.H. Kasai (Union Carbide, Tarrytown) had also used the ESR matrix technique to examine the intermetallic molecules Ag-M (M = Mg, Ca, Sr, Zn, Cd, and Hg) which he and his group had generated in argon matrices. Dr. R.H. Hauge (Rice University) employed both ESR and ir techniques in his examination of lithium metal reactions with H<sub>2</sub>O, CH<sub>3</sub>OH, and NH<sub>3</sub>.

Several papers on the topic of energy transfer in matrices were presented. Dr. L. Allamandola (Univ. of Leiden, Netherlands) and the group of J.W. Nibeler (Oregon State Univ.) described several elegant vibrational energy transfer studies of matrix-isolated C<sub>2</sub><sup>-</sup> as a function of concentration. Drs. H. Dubost, L. Abouf-Marguin, and the group of F. Legay (Univ. Paris Sud, Orsay, France) summarized their very elegant studies of vibrational relaxation in low-temperature matrices using ir laser excitation. These accounts were complemented by the theoretical studies of Dr. G. Zumofen (Lab. für Phys. Chemie, Zurich).

The application of magnetic circular dichroism in matrix isolation studies was presented by Dr. T.J. Barton (Univ. of East Anglia, England) and outlined (in experimental terms) in a poster session by Drs. E.R. Krausz, R.L. Mowery and P.N. Schatz (Univ. of Virginia). Dr. P. Barrett and his group at Univ. of California, Santa Barbara, described several Mössbauer studies of the iron-nitrogen molecule in solid nitrogen, while Dr. P.A. Montano (Univ. of West Virginia) outlined the general application of the matrix isolation technique to Mössbauer spectroscopy. In a related poster session, Dr. F.W. Froben (Freie Univ., Berlin) reported some exciting initial results of his attempts to stabilize active nitrogen intermediates in matrices. Dr. F.J. Litterst (Tech. Univ., Munich) also demonstrated that such species as <sup>57</sup>Fe, <sup>119</sup>Sn and <sup>151</sup>Eu<sup>+</sup>-halides can be examined in rare gas matrices via Mössbauer spectroscopy.

Dr. J. Pacansky of IBM (San Jose, Cal.) presented an informative lecture on the photolytic generation and characterization of alkyl radicals in low temperature matrices, while the more general topic of photoprocesses

in low-temperature matrices was discussed in a poster session monitored by Dr. A.J. Rest (Univ. of Southampton). One notable highlight along these lines was the first report of high resolution ir-matrix spectroscopy with tunable diode lasers by Dr. M. Dubs (Swiss Federal Institute, Zurich).

In an impromptu discussion, separate from the published list of presentations, Prof. D. White (Univ. of Pennsylvania) communicated the first report of the NMR spectrum of a molecule in a matrix.

Closing out the Conference were two separate reports of the study of chemiluminescent matrix reactions. Dr. J. Fournier and the group of Mme. C. Vermeil at the Centre National de la Recherche Scientifique (Paris) presented their results of a conventional examination of the thermoluminescence following uv irradiation of OCS trapped in a rigid matrix at 6 K. Dr. R.R. Smardzewski (Naval Research Laboratory, Washington, DC) had circumvented the numerous problems associated with conventional, single-channel photon counting by employing the novel technique of optical multichannel spectroscopy to an examination of the chemiluminescent matrix reactions of atomic oxygen, sulfur, chlorine, and  $O(^3P)+H_2S$ . He also pointed out the numerous pitfalls associated with the examination of chemiluminescent matrix reactions by conventional spectroscopic methods.

All things considered, the First International Conference on Matrix Isolation Spectroscopy proved to be both an informative and stimulating experience for each of the participating speakers and attendants.